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Mathematical models for correlating electrical parameters and milk adulterants

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Abstract

This work presents mathematical models obtained from electrical measurements to control of milk quality and detection of adulterations, especially by ethanol, sodium chloride and sodium bicarbonate. These substances may cause changes in the electrical properties of raw milk. Electrical measurements are non-destructive and fast techniques. The proposed models correlate the addition of the mentioned substances with measurements of conductance and phase angle at a fixed frequency of 100 Hz. Linear models were proposed from the data and the independence, normality, lack of adjustment and homoscedasticity were verified. The detection limits obtained based on conductance were 0.01 %, 0.03 g/L and 2.1 g/L for samples adulterated with ethanol, sodium chloride and sodium bicarbonate, respectively. The limits for measurements based on the phase angle were 0.4%, 1.3 g/L and 16.4 g/L, respectively. The results demonstrated that the proposed models may be a powerful tool to improve milk analysis methodologies.

Keywords: analysis methodology, electrical impedance, mathematical models, quality control, tampering milk.

1. Introduction

Traditionally, milk is considered a very important food, not only from a nutritional point of view, but also for its economic and social relevance. In this context, Brazil, in 2019, is among the largest milk producers and consumers in the world [1]. It has in its composition more than one hundred thousand constituents, being rich in proteins, carbohydrates, minerals and, vitamins [2]. Concerning its physical chemical parameters, the maximum and minimum limits are established by Normative Instructions [3].

The milk is constantly subjected to adulteration. This requires continuous care from the dairy industry and consumers to ensure its quality. Milk can be consumed raw or can also be used to produce various dairy products, such as cheese, sour cream, butter, among others.

Therefore, the entire dairy chain and consumers need efficient processes to guarantee product quality and safety [4]. Moreover, authenticity in food is also an important factor to

concern [5]. The adulterations aim oftentimes illicitly increase the milk volume being the one with water the most common [6]. Adding of chemicals to recover original standard parameters, also occur. Some of the techniques provided for in by legislation for assessing milk quality, for example, the freezing point (Crioscopia) [7] and density can be deceived by the simultaneous addition of water and restoratives such as sodium chloride and ethanol [8]. Substances as sodium bicarbonate, for example, can be used to recover Dornic acidity by masking reference techniques, such as the Dornic method [7]. Therefore, efficient methods to detect these substances are very important for the industry, being therefore the main motivation of this study.

There are numerous studies in the literature that discuss ways to detect different types of adulteration in milk [6, 8, 9, 10, 12,13]. However, the methods are often laborious, slow and expensive. In this context, mathematical models based on electrical measurements appear as an good alternative [14]. From an electrical point of view, milk can be understood as an electrolyte solution in which the charge transporters originate from the dissociation of salts. Therefore, the electrical conductance of milk is mainly attributed to the presence of ions, in particular Na^+ , K^+ and Cl^- [15]. Tampering, for example, causes a change in the electrical behavior of milk when subjected to an external excitation field.

Considering the phase angle measurements, few studies were found, as reported by Das et al [4]. Phase angle measurements are interesting, as they are stable and practically do not depend on the humidity and temperature [12]. Previous work by our group has indicated that conductance measures can be used as an alternative methodology to detect adulteration of milk by water [16].

In this work, statistical models have been proposed from conductance and phase angle measurements, focusing on its changes due to adulteration of ethanol, sodium chloride and sodium bicarbonate. This was done to establish a correlation between the results of the electrical measurement and the added substances. These models are important because, having this correlation, a methodology can be proposed to identify adulterations by these substances using these models. Statistical parameters were tested and evaluated in order to validate the proposed models.

2. Material and Methods

The experiments were performed with raw milk collected from Embrapa Dairy Cattle (José Henrique Bruschi Farm, located in Coronel Pacheco, Minas Gerais, Brazil) and also from industries in the Governador Valadares region of Minas Gerais, which have activities focused on the milk production chain. All raw milk samples were in accordance with Brazilian legislation [3], that is, with the following indices: acidity 14-18° Dornic, density of 1.028 g.mL⁻¹ to 1.032g.mL⁻¹ and maximum cryoscopic index of -0.530°H. Experiments were performed on samples of genuine raw milk and adulterated with ethanol absolute, sodium chloride and sodium bicarbonate.

All samples were prepared in 100 mL using 100 mL Erlenmeyer flasks. For the weighing was used an analytical balance Shimadzu AY brand model 220, with an accuracy of 0.001g. The order for measurements was by aleatory.

Samples with ethanol additions were prepared at levels 0, 5, 10, 15, 20, 25 and 30 %(v/v).

The ethanol it acts as a reconstituting agent, aiming to reestablish the milk's standard characteristics, which are altered when it is adulterated with water. In Brazil, milk is adulterated with a high levels of water. Adulteration with sodium bicarbonate was performed from 0 to 0.3% (w/v) in additions of 0.05% (w/v). Adulteration with sodium chloride was performed samples from 0 to 0.15% (w/v) in additions of 0.025% (w/v). All samples were prepared in six replications and seven levels of concentration, totalizing therefore 42 points for each adulteration studied.

The electrical conductance and phase angle were obtained using an impedance analyzer HIOKI, model IM3570 excited by signal alternated (AC) of 1V peak-to-peak, adapted with eletrode of parallel plates (geometric constant $K = 1 \text{ cm}^{-1}$) for liquids measurements, as shown in Figure 1. In all experiments the temperature (20°C) and the humidity were kept constant. The frequency set specifically at 100Hz is intended to facilitate the technological assembly of signal generation.

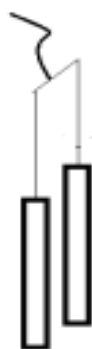


Figure 1: Simplified diagram of the geometry of a cell for measurements in liquids.

3. Results and Discussion

Milk has electrical properties due to the presence of ionic compounds such as salts. The overall milk conductivity depends on the distribution of salt fractions between the soluble and colloidal phase angles [17]. Moreover, the variations in the fat globule size and the structure of the casein, which controls the solubilization of the colloidal salts need to be taken into account. The addition of non-ionic adulterants (as is the case of water, ethanol) may inhibit efficient mass transfer in milk, decreasing the conductance and phase angle. The delay between the external excitation electrical signal and the electrical response are measured by the phase angle. If acidic or basic adulterants are added to milk, the dissolved ionic content changes. The acidity of milk affects the protein coagulation thereby releasing mineral salts to the colloidal phase. The electrical behavior of milk increase or decrease in dissolved ionic content in the serum depending upon formation or dissolution of protein particles [14].

The results obtained demonstrated that the dilutions with ethanol reduced the conductance and phase angle. This was due to the decrease in the concentration of charge carriers in the milk. For the samples of milk added with chloride and sodium bicarbonate, the conductance and phase angle have increased. The results obtained in this work are similar with those of Mabrook and Petty, which investigated water addition as a function of frequency by means of conductance measurements [18].

The results present linear variations for all the dilutions. The mathematical models for this correlation are described in Table 1 and will be discussed.

3.1. Statistical models

The regression models were obtained using the least squares method. The results are shown in Table 1 and were described using the inverse functions, with the variable X representing the electrical measure (conductance or phase angle) and variable Y the quantification of the detected adulterant. This was described thus, to emphasize the proposed methodology, that is, from the measured analytical signals and using the found models, adulterations can be detected.

Adulterant		Linear fit model	Limit of detection (LOD) Limit of quantification (LOQ)
Sodium chloride	Conductance	$Y = (0.7847 \pm 0.0004) X + (-1.2754 \pm 0.0006)$	LOD 0.0271 g/L
			LOQ 0.0821 g/L
	phase angle	$Y = (0.02020 \pm 0.00002) X + (-0.7639 \pm 0.0008)$	LOD 1.3160 g/L
			LOQ 3.9877 g/L
Sodium bicarbonate	Conductance	$Y = (3.1 \pm 0.1) X + (-5.0 \pm 0.2)$	LOD 2.1 g/L
			LOQ 6.2 g/L
	phase angle	$Y = (0.0477 \pm 0.0006) X + (-1.90 \pm 0.02)$	LOD 16.38 g/L
			LOQ 49.64 g/L
Ethanol	Conductance	$Y = (-41.6 \pm 0.1) X + (67.4 \pm 0.2)$	LOD 0.01 %
			LOQ 0.04 %
	phase angle	$Y = (-1.65648 \pm 0.00581) X + (63.9 \pm 0.2)$	LOD 0.4 %
			LOQ 1.1 %

Table 1: Models for average values of conductance and phase angle for the additions of ethanol, Sodium Chloride and Sodium Bicarbonate.

Naturally, the limits of detection (LOD) are lower than the limits of quantification (LOQ), however, it is noteworthy that in all models the evaluated limits were lower for conductance measurements in relation to the phase angle. This indicates that the methodology based on conductance measurements presents greater sensitivity for the analysis. The models also showed that the LOD and LOQ calculated for the addition of sodium chloride are lower than those with sodium bicarbonate, indicating that there is a greater sensitivity of the proposed methodology for the detection of these chlorides. This is due to the nature of the charge carriers dissociated. In the case of sodium chloride, the chlorine and sodium ions are light and with a significant charge, therefore, high ion mobility, which causes a strong change in the electrical

characteristics of the medium. For correlation models with ethanol additions, small limits of detection and quantification were also observed, since the conductive nature of ethanol is very low in relation to milk and therefore additions will significantly vary these measured properties. The proposed methodology will, therefore, be able to identify low levels of this type of adulteration.

Statistical tests were carried out to validate the proposed models. The results are shown in Table 2. The assumptions of normality, homoscedasticity and independence were evaluated. The coefficient of determination (R^2) and the model's lack of fit test were also calculated.

Adulterant	Electrical Measurement	(R^2)	Test	p-value
Sodium Chloride	Conductance	0.999	Normality: Shapiro-Wilk	0.37
			Homoscedasticity: Goldfeld Quandt	0.49
			Independence	0.62
			Lack of fit	0.62
	phase angle	0.999	Normality: Shapiro-Wilk	0.94
			Homoscedasticity: Goldfeld Quandt	0.18
			Independence	0.21
			Lack of fit	0.99
Sodium Carbonate	Conductance	0.946	Normality: Shapiro-Wilk	0.16
			Homoscedasticity: Goldfeld Quandt	0.49
			Independence	0.92
			Lack of fit	0.89
	phase angle	0.994	Normality: Shapiro-Wilk	0.29
			Homoscedasticity: Goldfeld Quandt	0.44
			Independence	0.15
			Lack of fit	0.71
Ethanol	Conductance	0.999	Normality: Shapiro-Wilk	0.41
			Homoscedasticity: Goldfeld Quandt	0.36
			Independence	0.71
			Lack of fit	0.12
	phase angle	0.999	Normality: Shapiro-Wilk	0.24
			Homoscedasticity: Goldfeld Quandt	0.098
			Independence	0.023
			Lack of fit	0.26

Table 2: Models for average values of conductance and phase angle for the frauds with addition of ethanol, Sodium Chloride and Sodium Bicarbonate. R^2 are the corresponding correlation coefficients.

4. Conclusions

This work presented mathematical models of correlation among electrical measurements and substances added in milk (ethanol, sodium chloride and sodium bicarbonate). The models presented a coefficient of determination (R^2) greater than 0.94, which indicates that there is good adjustment of the proposed models. In addition, statistical tests were performed to validate the robustness of the proposed models. The detection limits obtained based on conductance were 0.01%, 0.03 g/L and 2.06 g/L for samples adulterated with ethanol, sodium chloride and sodium bicarbonate, respectively, while those obtained based in the phase angle were 0.35%, 1.32 g/L and 16.38 g/L, respectively. Therefore, based on the results presented, it is possible to propose a methodology for analysis milk and identifying adulterations using the models described in this work.

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